

SCIENCE FOR CERAMIC PRODUCTION

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CERAMICS BASED ON BORON NITRIDE OBTAINED BY REACTION-BASED SINTERING

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Reaction-based sintering of ceramics based on hexagonal boron nitride is investigated. It is found that the use of presintered aluminum nitride milled to the particle size of 45–125 μm is significantly more efficient than using finely disperse boron nitride or coarsely disperse aluminum nitride as the inert filling agent.

Hexagonal boron nitride is characterized by a number of valuable insulating properties and high chemical inertness and is a promising high-refractory compound for ceramic production. However, due to its structural specifics, the manufacture of boron nitride ceramic articles of complex configuration and sufficiently high strength parameters using such up-to-date methods as slip casting, explosive and hot compression, and precipitation from the gas phase [1, 2] involves high costs and difficulty due to the high sinterability and low strength of boron nitride ceramics.

The use of the reaction sintering method for ceramics based on boron nitride can solve this problem. It is known [3–5] that the consolidation of a ceramic sample in reaction-based sintering is mostly determined by chemical reactions and not only by physical processes, as in solid-phase and liquid-phase sintering. The contemporary theory in [6] adequately describes reaction-based sintering in the $\text{SiC} - \text{Si} - \text{C}$ and $\text{Si}_3\text{N}_4 - \text{Si}$ systems.

Paper [3] reports the use of the reaction sintering method to produce boron nitride ceramics exhibiting high compressive strength of 120–150 MPa (whereas the bending strength is about 50 MPa) within the temperature interval from 20 to 1400–1500°C and stable dielectric properties: dielectric constant ≈ 3.3 ; dielectric loss tangent > 10 . The obtained large products (50–60 cm high, 15–20 cm in diameter) made of boron nitride had a total porosity of 25–30% and a sufficiently low thermal coefficient of linear expansion (TCLE) equal to $0.3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

The study in [1] concerns an investigation of the materials obtained by sintering in nitrogen of samples made of mixtures of pure boron and aluminum nitrides, boron nitride with

aluminum, and aluminum nitride with boron. The sintering of BN + Al mixtures does not lead to positive results, since the nitrides dissociate at temperatures significantly lower than those needed for sintering, regardless of the increase in the nitrogen pressure. Much better results were obtained in nitrogen treatment of AlN + B mixtures, which is reaction-based sintering of the initial aluminum nitride with the boron nitride formed in nitrogen treatment.

In the general case, the variations in the total porosity or relative density are taken as the extent of reaction-based sintering in production of multiphase composite materials. However, for the unique evaluation of different chemical reactions with respect to possible volume variations, a unified generalized criterion is used, i.e. the volume effect of the reaction (VER) [6]. The VER is a constant value for each chemical reaction, and under the conditions of constant dimensions of the heated body, absence of uncontrollable mass loss through evaporation and dissociation, as well as side reactions, the VER is calculated from the following equations:

$$\delta = (v_f/v_i - 1) \times 100;$$

$$\delta = (M_f \gamma_f / M_i \gamma_i - 1) \times 100;$$

$$\alpha = 1 + \delta/100 = v_f/v_i;$$

$$P_f = P_i - \delta(1 - P_i/100);$$

$$K_f = K_i(1 + \delta/100) = \alpha K_i,$$

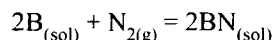
where δ is the volume effect of the reaction, %; v_i and v_f are the molar volumes of the initial and the final products, cm^3/mole ; M_i and M_f are the molar masses of the initial and

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the final products, g/mole; α is a relative criterion similar to the VER; γ_i and γ_f are the true densities of the initial and the final products, g/cm³; P_i and P_f are the initial and the final porosity of the sample; K_i and K_f are the initial and the final relative density of the sample, %.

The interrelationship between these parameters is graphically illustrated in Fig. 1.

The investigated reaction



is distinguished by a very high VER ($\alpha = 2.36$, $\delta = 136\%$). As can be seen from Fig. 1, the minimum initial porosity of the sample in this case is about 58%, whereas the strength of this low-density sample is insufficient for high-temperature firing. Therefore, according to reaction sintering theory, in order to reduce the VER, it is necessary to introduce an inert filler (BN, AlN, or SiC) in the initial mixture.

In our investigation we used black-brown amorphous boron (particle size $\sim 3 \mu\text{m}$). The following compounds were chosen as inert fillers:

- α -boron nitride with the average particle size $\sim 10 \mu\text{m}$ (samples 0 – 6)
- standard industrially synthesized AlN powder (samples 13 – 22 and samples AO);
- aluminum nitride previously sintered and crushed to 45 – 125 μm particles (samples 7 – 12).

In order to investigate the effect of the particle size of the inert filler on the properties of reaction-sintered ceramics, samples 13 – 17 were made of AlN with a particle size $< 125 \mu\text{m}$, and samples 18 – 22 were prepared from AlN with a particle size of 125 – 250 μm .

The initial mixture compositions (B + BN + AlN) were calculated from the above quoted equations, based on the initial sample density which would meet the optimum conditions of reaction-based sintering ($P_f = 0$) and at the same time provide for the required strength of the initial sample. For this purpose, the moldability of B + BN (1 : 2) and B + AlN

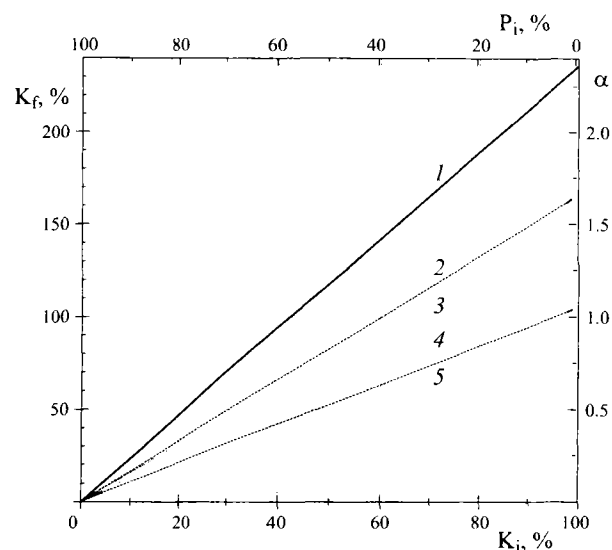


Fig. 1. Area of investigation of reaction-based sintering: 1) 100 B (here and elsewhere wt.%) without inert filler; $\delta = 146\%$; 2) 40 B = 60 AlN, $\delta = 65\%$; 3) 40 B + 60 BN, $\delta = 53\%$; 4) 25 B + 75 BN, $\delta = 33\%$; 5) 5 B + 95 AlN, $\delta = 9\%$ (the studied area of reaction-based sintering in the BN – B system is limited by curves 3 and 4, and in the AlN – B system it is limited by curves 2 and 5).

(1 : 3) mixtures were investigated and the optimum values of the molding pressure were chosen corresponding to the respective values of the initial sample porosity.

Therefore, broad composition spectra containing from 25 to 40 wt.% boron in the initial mixture with boron nitride and from 5 to 40% boron in the initial mixture with aluminum nitride were selected for investigation (Fig. 1). For reference, samples 0 (100% BN) and samples AO (100% presintered AlN) were prepared without boron, and samples B were prepared with 100% boron content.

The molded disk-shaped samples 14 mm in diameter prepared for reaction-based sintering were first dried for 1.5 h at the temperature of 100°C to remove excess moisture. The thermal treatment of the samples (reaction-based

TABLE 1

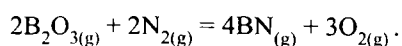
Sample	Before firing				After firing			
	boron content, wt. %	apparent density, g/cm ³	porosity, %	apparent density, g/cm ³	porosity, %	depth of reaction-based sintering, %	linear shrinkage, %	volume expansion, %
1	40	1.41 ± 0.06	39.0 ± 2.4	1.09 ± 0.04	52.3 ± 1.8	37 ± 17	12.4 ± 0.5	81 ± 8
2	36	1.41 ± 0.03	38.9 ± 1.3	1.00 ± 0.07	56.2 ± 0.1	34 ± 12	11.3 ± 1.0	57 ± 5
3	32	1.43 ± 0.02	37.9 ± 1.0	1.08 ± 0.07	53.0 ± 2.9	34 ± 14	13.1 ± 0.7	62 ± 1
4	29	1.45 ± 0.03	37.0 ± 1.2	0.98 ± 0.02	57.1 ± 0.8	31 ± 13	14.1 ± 1.0	69 ± 7
5	27	1.43 ± 0.01	38.1 ± 0.3	0.96 ± 0.04	58.1 ± 1.6	39 ± 2	14.1 ± 0.2	80 ± 3
6	25	1.42 ± 0.01	38.4 ± 0.5	0.96 ± 0.04	58.9 ± 1.9	38 ± 3	14.1 ± 0.6	77 ± 1
0	0	1.49 ± 0.00	34.9 ± 0.2	1.01 ± 0.03	55.8 ± 1.5	—	3.1 ± 0.3	27 ± 1
B	100	1.23 ± 0.01	47.6 ± 0.3	1.39 ± 0.07	39.2 ± 3.0	46 ± 3	12.6 ± 1.6	56 ± 10

TABLE 2

Sample	Before firing			After firing					
	boron content, wt. %	apparent density, g/cm ³	porosity, %	boron content, wt. %	apparent density, g/cm ³	porosity, %	depth of reaction-based sintering, %	linear shrinkage, %	volume expansion, %
7	40	1.88 ± 0.01	33.4 ± 0.2	46	1.80 ± 0.09	33.9 ± 3.4	38 ± 7	6.0 ± 0.7	38 ± 6
8	36	1.94 ± 0.01	32.5 ± 0.4	42	1.89 ± 0.04	31.7 ± 1.5	25 ± 2	6.2 ± 0.5	31 ± 4
9	32	1.97 ± 0.01	32.2 ± 0.3	38	1.92 ± 0.02	31.8 ± 0.7	34 ± 5	5.9 ± 1.1	33 ± 5
10	29	2.01 ± 0.01	31.4 ± 0.2	35	1.93 ± 0.04	32.1 ± 1.3	25 ± 5	5.1 ± 0.6	27 ± 2
11	27	2.04 ± 0.01	30.9 ± 0.3	32	1.99 ± 0.03	30.9 ± 1.0	33 ± 6	5.1 ± 0.6	20 ± 3
12	25	2.05 ± 0.01	31.0 ± 0.4	30	2.06 ± 0.03	28.8 ± 1.0	27 ± 7	4.8 ± 0.5	20 ± 3
13	25	1.75 ± 0.01	41.3 ± 0.4	30	1.18 ± 0.01	59.3 ± 0.3	50 ± 1	19.0 ± 0.3	73 ± 2
14	20	1.75 ± 0.01	42.3 ± 0.2	24	1.26 ± 0.02	57.3 ± 0.8	48 ± 5	14.9 ± 0.0	55 ± 1
15	15	1.78 ± 0.01	42.4 ± 0.2	19	1.42 ± 0.01	53.4 ± 0.2	39 ± 10	10.2 ± 0.3	35 ± 2
16	10	1.82 ± 0.01	42.3 ± 0.3	13	1.70 ± 0.02	45.1 ± 0.6	37 ± 10	3.7 ± 0.3	12 ± 1
17	5	1.79 ± 0.01	44.0 ± 0.2	6	1.89 ± 0.01	40.3 ± 0.0	-1 ± 6	-1.6 ± 0.3	-5 ± 0
18	25	1.73 ± 0.00	41.9 ± 0.0	30	1.08 ± 0.01	62.7 ± 0.5	46 ± 5	22.0 ± 0.5	84 ± 2
19	20	1.77 ± 0.01	41.7 ± 0.4	24	1.18 ± 0.03	60.1 ± 0.9	41 ± 7	17.7 ± 0.5	65 ± 2
20	15	1.79 ± 0.01	42.0 ± 0.3	19	1.29 ± 0.02	57.6 ± 0.7	36 ± 11	13.9 ± 0.3	49 ± 0
21	10	1.80 ± 0.01	42.7 ± 0.4	13	1.60 ± 0.02	49.2 ± 0.4	36 ± 7	6.4 ± 0.0	20 ± 1
22	5	1.83 ± 0.00	42.9 ± 0.1	6	1.87 ± 0.03	41.2 ± 0.5	-22 ± 11	-0.9 ± 0.3	-3 ± 1
AO	0	2.03 ± 0.02	37.8 ± 0.5	0	1.93 ± 0.17	41.0 ± 5.1	-	0.0 ± 4.2	-2 ± 8

sintering) was performed at the temperature of 1850°C for 2.5 h in a tunnel furnace in a flow of gaseous nitrogen.

The data of the x-ray phase analysis performed after sintering prove that the reaction of boron with nitrogen was completed in all samples, and the samples did not contain any boron that has not reacted. However, the increase in the sample mass did not exceed 50% of the theoretical value, and the mass of the boron-free samples decreased in firing by 5–10%, i.e., a loss of the inert filler mass was observed. This phenomenon can have the following explanation. At such high firing temperatures, aluminum nitride and especially boron nitride have perceptible volatility, and part of them is sublimated. The boron nitride and boron used in the experiment contain B₂O₃ which is x-ray amorphous and cannot be identified by x-ray phase analysis. This compound is extremely low-melting and at the temperature of reaction-based sintering, it evaporates from the sample into the gas phase where it reacts with nitrogen according to the following reaction:



The aluminum nitride used in the investigation contains AlON oxynitride which was identified by x-ray phase analysis; the action of AlON is similar to that of B₂O₃.

The results of sintering of the B–BN system samples revealed that they were not compacted in reaction-based sintering as expected; on the contrary, their volume expanded

(Table 1), which contradicted the chemical sintering theory. All samples exhibited low compressive strength (~10 MPa), which is determined by the presence of cracks and pores.

It is difficult to explain these results in the context of reaction-based sintering, since the condition of the constant dimensions of the system was not satisfied, and uncontrollable mass losses were observed. The substantial increase in the sample volume in this case was probably caused not by the fact that the volume effect of the reaction exceeded the accessible open porosity of the sample but rather by loosening of the initial sample (sample 0) owing to the recrystallization of particles at high temperatures.

Another reason for the decrease in ceramic density can be the nature of the mutual arrangement of B and BN particles at the microlevel. It is known that filling of the initial sample pores with reaction products in the course of the chemical reaction can take place only if fine boron particles are located inside larger pores and cavities [7]. In our case, the average ratio of the average sizes of boron nitride and boron particles was ~3. The study of the sample microstructure revealed that the majority of B particles are located between BN particles without having sufficient space for free growth, and their increase in size in the course of reaction-based sintering inevitably forces apart the particles of the inert initial nitride and consequently causes expansion and loosening of the material. This assumption is supported by the fact that the closed porosity of boron nitride ceramics after firing was 2–6%, whereas the open porosity was 50%.

The results of firing of samples of the B – AlN system are given in Table 2. The same picture as in the B – BN samples was observed in samples 13 – 16 and 18 – 21 as well. It is obvious that the increase in the density of samples 17 and 22 was due to the shrinkage of the initial AlN, i.e., the usual sintering. The compaction of samples 7 – 12 made of presintered AlN was determined by reaction-based sintering accompanied with the formation of secondary BN. In spite of significant volume expansion, the total porosity of these samples remained at the level of 30%. The compaction caused by reaction-based sintering is also confirmed by the nature of the porosity of the specified samples after firing.

It should be noted that the firing results revealed substantial differences between the behavior of standard and presintered AlN in the conditions of high-temperature reaction-based sintering. The presintered AlN proved to be more stable than the AlN without preliminary heat treatment, which is indicated by the linear shrinkage of the samples of the B-AlN system (Table 2). It should be noted as well that the samples of the presintered AlN are much more moldable. After molding, the apparent density of samples 12 was 2.05 g/cm³, and that of samples 13 was 1.75 g/cm³.

The study of the effect of dispersion of the initial inert filler AlN revealed the uselessness of coarse-grained powders with a particle size above 125 μm. The compressive strength of samples 18 – 21 did not exceed 15.9 MPa and was a factor of 2 – 5 lower than in samples 13 – 17 having a similar composition and dispersion of 125 μm. Among samples 13 – 17, the highest compressive strength (37.4 MPa) was exhibited by samples 17. The mechanical strength of the samples made of presintered aluminum nitride ranged from 25.1 MPa (samples 7) to 53.6 MPa (sample 12).

The specific volume electric resistance and the dielectric constant of the fired samples 0 – 6 amounted to $(10 \pm 4) \times 10^{10} \Omega \cdot \text{cm}$ and 3.5 ± 0.5 , respectively, and for samples 7 – 22 these values were $(12 \pm 5) \times 10^{10} \Omega \cdot \text{cm}$ and 7.3 ± 0.8 , respectively.

As a consequence of the performed study, the following conclusions can be made:

the use of finely disperse hexagonal boron nitride as an inert filler for decreasing a very high VER is not efficient;

the use of aluminum nitride is more promising, since it does not expand at high firing temperatures as α-BN does; and the use of presintered AlN is much more efficient than ordinary AlN without heat treatment.

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